PATENT SPECIFICATION

Inventors: GODFREY WINTERS and JOHN SHELMERDINE

777,961

Date of filing Complete Specification: May 23, 1955.

Application Date: July 14, 1954. *No. 20535/54.*

Complete Specification Published: July 3, 1957.

Index at acceptance:—Class 2(3), C3A13B2(A1: A2: A3: E).

International Classification:—C07c.

COMPLETE SPECIFICATION

Improvements relating to the Desulphurisation of Phenolic Materials

We, BRITISH TAR PRODUCTS LIMITED, a British Company, of Hayes Road, Cadishead, near Manchester, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the desulphurisation of phenolic materials, and has for its object to provide a process whereby sulphur can be removed from phenolic materials more efficiently and easily than by known methods, and further to provide a process in which reduction of phenolic hydroxyl groups of the feedstock is avoided and in which regeneration of catalyst is required only infrequently.

According to the invention the phenolic material in the vapour phase, together with hydrogen, is passed over a metal oxide or metal salt catalyst at an elevated temperature, whereby sulphur is removed from sulphur compounds present as impurities and is converted to hydrogen sulphide.

Most of the hydrogen sulphide passes on with the unused hydrogen, from which it may be removed by conventional means, such as scrubbing with caustic soda liquor, or absorption in iron oxide beds. Any small amount of hydrogen sulphide remaining dissolved in the liquid product after condensation may be removed by air blowing. The unused and purified hydrogen is recycled.

A suitable catalyst is a mixture of the oxides of cobalt and molybdenum, or cobalt molybdate, either alone or incorporated with a support such as alumina. Under working conditions, the catalyst reacts to some extent with hydrogen sulphide, so that the oxygen is partly replaced by sulphur, this partial replacement leading to an increase in catalyst activity. After prolonged use, the catalyst can be regenerated by conventional means, such as steam and air blowing.

[*Price 3s. 6d.*]

The space velocity of the feed is varied according to the degree of desulphurisation required, the kind of feed stock and catalyst activity. The temperature required will depend on the kind of feed stock, but in most cases will be between 200 and 300°C. The pressure should be such that no reduction of the phenol hydroxyl groups occurs, and will usually be below 3 atmospheres absolute.

The accompanying drawing shows diagrammatically and by way of example an arrangement of plant suitable for carrying out the invention.

The feedstock is pumped by a pump 1 into a preheater and vapouriser 2. The resulting vapours, together with hydrogen supplied through pipe 8, are passed through a reactor 3 containing the catalyst whereby the sulphur contained in organic sulphur compounds is converted into H_2S, and through a condenser 4 to a disengager 5 in which the liquid products are deposited, while the gases pass to a purifier 6 in which H_2S is absorbed and from which hydrogen is recycled by a compressor 7 to the reactor 3, bleed off of hydrogen being arranged if necessary at 9. The desulphurised phenolic materials are withdrawn from the disengager at 10.

Examples of the process according to the invention are as follows:

The space velocities are given in volumes per volume of catalyst per hour, the volumes being measured at normal temperature for the liquids and at normal temperature and pressure for the hydrogen.

EXAMPLE 1.

40/42% commercial metacresol containing 0.08% sulphur is treated at an average temperature of 233°C with hydrogen at normal atmospheric pressure, over a catalyst consisting of cobalt molybdate on alumina. The liquid space velocity is 0.5 V/V/hr. and the hydrogen space velocity is 150 V/V/hr. The

sulphur content of the product is 0.01%. The process can be continued for 60 hours with no fall off in catalyst activity.

EXAMPLE 2.

The feedstock is 40/42% commercial metacresol containing 0.032% sulphur. This is treated with hydrogen at atmospheric pressure and 240°C over cobalt molybdate on alumina, the liquid space velocity being 0.5 V/V/hr, and the hydrogen space velocity 150 V/V/hr. The sulphur content of the product is 0.01%.

EXAMPLE 3.

Commercially pure ortho-cresol containing 0.064% sulphur is treated with hydrogen at atmospheric pressure and 246°C over cobalt molybdate on alumina, with a liquid space velocity of 0.25 V/V/hr. and a hydrogen space velocity of 300 V/V/hr. The sulphur content of the product is 0.012%.

EXAMPLE 4.

A mixture of xylenols, boiling range 205—225°C., containing 0.042% sulphur is treated with hydrogen at atmospheric pressure and 300°C. over cobalt molybdate on alumina, with a liquid space velocity of 0.25 V/V/hr. and a hydrogen space velocity of 300 V/V/hr. The sulphur content of the product is 0.007%.

What we claim is:—

1. A method of desulphurising phenolic materials, in which the phenolic material in the vapour phase, together with hydrogen, is passed over a metal oxide or metal salt catalyst at an elevated temperature, whereby sulphur is removed from sulphur compounds present as impurities and is converted to hydrogen sulphide.

2. A method as claimed in claim 1, in which the catalyst is a mixture of cobalt and molybdenum oxides or a cobalt molybdate, either alone or incorporated with a support such as alumina.

3. A method as claimed in claim 1 or 2, in which the temperature used is from 200 to 300°C.

4. A method as claimed in claim 1, 2 or 3, in which the phenolic material is vapourised and then mixed with hydrogen and passed over the catalyst, the desulphurised liquid product being separated by condensation from the unused hydrogen and hydrogen sulphide, the hydrogen being recycled after being freed from hydrogen sulphide.

5. A method of desulphurising phenolic materials, substantially as described.

MARKS & CLERK.

PROVISIONAL SPECIFICATION

Improvements relating to the Desulphurisation of Phenolic Materials

We, BRITISH TAR PRODUCTS LIMITED, a British Company, of Hayes Road, Cadishead, near Manchester, do hereby declare this invention to be described in the following statement:—

This invention relates to the desulphurisation of phenolic materials, and has for its object to provide a process whereby sulphur compounds can be removed from phenolic materials more efficiently and easily than by known methods, and further to provide a process in which breakdown of the feedstock is avoided and in which regeneration of catalyst is required only infrequently.

According to the invention the phenolic material in the vapour phase, together with hydrogen, is passed over a catalyst at an elevated temperature, whereby sulphur compounds are converted to hydrogen sulphide.

Most of the hydrogen sulphide passes on with the unused hydrogen, from which it may be removed by conventional means, such as scrubbing with caustic soda liquor, or absorption in iron oxide beds. Any small amounts of hydrogen sulphide remaining dissolved in the liquid product after condensation may be removed by air blowing.

A suitable catalyst is a mixture of the oxides of cobalt and molybdenum, or a chemical compound of cobalt, molybdenum and oxygen, either alone or incorporated with a support such as alumina. Under working conditions, the catalyst reacts to some extent with hydrogen sulphide, so that the oxygen is partly replaced by sulphur, this partial replacement leading to an increase in catalyst activity. After prolonged use, the catalyst can be regenerated by conventional means, such as steam and air blowing.

The space velocity of the feed is varied according to the degree of desulphurisation required, the kind of feed stock and catalyst activity. The temperature required will depend on the kind of feed stock, but in most cases will be between 200 and 300°C. Hydrogen pressure is maintained by recycling and should be such that no breakdown of the phenol hydroxyl groups occurs.

The feedstock may be pumped into a preheater and vapouriser, the resulting vapours being mixed with hydrogen and passed through a reactor containing the catalyst to a disengager in which the liquid products are condensed, while the gases pass to a purifier, from which hydrogen is recycled to the reactor inlet, makeup or bleed off being arranged as necessary.

An example of the process according to the invention is as follows: 40/42% commercial metacresol containing 0.08% sulphur is treated

at an average temperature of 233°C with hydrogen at a pressure of one atmosphere, over a catalyst consisting of cobalt molybdate on alumina. The liquid space velocity is 0.5 V/V/hr. and the hydrogen space velocity is 150 V/V/hr. The sulphur content of the product is 0.01%. The process can be continued for 60 hours with no fall off in catalyst activity.

The space velocities are given in volumes per volume of catalyst per hour, the volumes being measured at normal temperature for the liquids and at normal temperature and pressure for the hydrogen.

MARKS & CLERK.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1957.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

777961 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*